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⑤④ **METAL-CONTAINING SPINEL COMPOSITION AND PROCESS OF USING SAME.**

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## Description

This invention relates to improved metal-containing spinel compositions, particularly for use in a manner to effect a reduction in the emission of sulfur oxides and/or nitrogen oxides to the atmosphere. In one specific embodiment, the invention involves compositions and processes for the catalytic cracking of sulfur-containing hydrocarbon feedstocks to effect a reduction in the amount of sulfur oxides and/or nitrogen oxides emitted from the regeneration zone of a hydrocarbon catalytic cracking unit.

Typically, catalytic cracking of hydrocarbons takes place in a reaction zone at hydrocarbon cracking conditions to produce at least one hydrocarbon product and to cause carbonaceous material (coke) to be deposited on the catalyst. Additionally, some sulfur, originally present in the feed hydrocarbons, may also be deposited, e.g., as a component of the coke, on the catalyst.

Sulfur-containing coke deposits tend to deactivate cracking catalyst. Cracking catalyst is advantageously continuously regenerated, by combustion with oxygen-containing gas in a regeneration zone, to low coke levels, typically below about 0.4% by weight, to perform satisfactorily when it is recycled to the reactor. In the regeneration zone, at least a portion of the sulfur, along with carbon and hydrogen, which is deposited on the catalyst, is oxidized and leaves in the form of sulfur oxides (sulfur dioxide and sulfur trioxide, hereinafter referred to a "SOx") along with substantial amounts of carbon monoxide, carbon dioxide and water. At least a portion of the nitrogen, which may be present in the coke deposits and/or in the oxygen-containing gas, is oxidized at the conditions in the regeneration zone to nitrogen oxides which also leave with the flue gas from the regeneration zone.

Considerable recent research effort has been directed to the reduction of sulfur oxide and nitrogen oxide atmospheric emissions, e.g., from the regeneration zones of hydrocarbon catalytic cracking units. One technique that has been suggested for reducing such sulfur oxide emissions involves circulating one or more metal oxides capable of associating with oxides of sulfur with the cracking catalyst inventory in the regeneration zone. When the particles containing associated oxides of sulfur are circulated to the reducing atmosphere of the cracking zone, the associated sulfur compounds are released as gaseous sulfur-bearing material such as hydrogen sulfide, which is discharged with the products from the cracking zone and is in a form which can be readily handled in a typical facility, e.g., petroleum refinery. The metal reactant is regenerated to an active form, and is capable of further associating with the sulfur oxides when cycled to the regeneration zone.

A metallic component, either incorporated into catalyst particles or present on any of a variety of "inert" supports, is exposed alternately to the oxidizing atmosphere of the regeneration zone of an FCCU and the reducing atmosphere of the cracking zone to reduce sulfur oxide emissions from regenerator gases in accordance with the teachings of U.S. Patents Nos. 4,153,534 and 4,153,535 to Vasalos and Vasalos, et al., respectively. In Vasalos, et al., a metallic oxidation promoter, consisting of components of ruthenium, rhodium, palladium, platinum, osmium, iridium, platinum, vanadium, uranium, zirconium, rhenium, silver and mixtures thereof is also present when carbon monoxide emissions are to be reduced. Vasalos, et al., teaches that the more preferred metallic promoter consists of components of ruthenium, rhodium, palladium, osmium, iridium, platinum and rhenium. These patents disclose nineteen different metallic components, including materials as diverse as alkaline earths, sodium, heavy metals and rare earth, as being suitable reactants for reducing emissions of oxides of sulfur. The metallic reactants that are especially preferred are sodium, magnesium, manganese and copper. The carriers for the metallic reactants, preferably have surface areas of at least 50 square meters per gram. Examples of allegedly "inert" supports are silica, alumina and silica-alumina. The Vasalos and Vasalos, et al., patents further disclose that when certain metallic reactants (exemplified by oxides of iron, manganese or cerium) are employed to capture oxides of sulfur, such metallic components can be in the form of a finely divided fluidizable powder.

A vast number of sorbents have been proposed for desulfurization of non-FCCU flue gases in zones outside the unit in which SOx is generated. In some such non-FCCU applications, the sorbents are regenerated in environments appreciably richer in hydrogen than the cracking zone of an FCC unit. Fifteen adsorbents are disclosed for flue gas desulfurization in a publication of Lowell, et al., "SELECTION OF METAL OXIDES FOR REMOVING SOx FROM FLUE GAS," Ind. Eng. Chemical Process Design Development, Vol. 10, Nov. 3, 1971. In U.S. Patent No. 4,001,375 to Longo, cerium on an alumina support is used to absorb SO2 from non-FCCU flue gas streams or automobile exhaust at temperatures of 572 to 1472 degrees F., preferably 932 to 1100 degrees F.

D. W. Deberry, et al., "RATES OF REACTION OF SO2 WITH METAL OXIDES," Canadian Journal of Chemical Engineering, 49, 781 (1971) reports that cerium oxide was found to form sulfates more rapidly than most of the other oxides tested. The temperatures used, however, were below 900 degrees F. and thus below those preferred for use in catalyst regenerators in FCC units.

Many commercial zeolitic FCC catalyst contain up to 4% rare earth oxide, the rare earth being used to stabilize the zeolite and provide increased activity. See, for example, U.S. Patent No. 3,930,987 to Grand. The rare earths are most often used as mixtures of  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$  and others. Some catalyst is produced by using a lanthanum-rich mixture obtained by removing substantial cerium from the mixture of rare earth. It has been found that the mere presence of rare earth in a zeolitic cracking catalyst will not necessarily reduce  $\text{SO}_x$  emissions to an appreciable extent.

In accordance with the teachings of U.S. Patent No. 3,823,092 to Gladrow, certain zeolitic catalyst compositions capable of being regenerated at a rate appreciably faster than prior art rare earth exchanged zeolitic catalyst compositions are produced by treating a previously rare earth exchanged zeolitic catalyst composition with a dilute solution containing cerium cations (or a mixture of rare earths rich in cerium). The final catalysts contain 0.5 to 4% cerium cations which are introduced to previously rare earth exchanged zeolitic catalyst particles prior to final filtering, rinsing and calcining. Cerium is described as an "oxidation promoter".

Thus, considerable amount of study and research effort has been directed to reducing oxide of sulfur emissions from various gaseous streams, including those from the stacks of the regenerators of FCC units. Many metallic compounds have been proposed as materials to pick up oxides of sulfur in FCC units (and other desulfurization applications). Many of the proposed metallic compounds or reactants lose effectiveness when subjected to repeated cycling. Thus, when Group II metal oxides are impregnated on FCC catalysts or various supports, the activity of the Group II metals is rapidly reduced under the influence of the cyclic conditions. Discrete alumina particles, when combined with silica-containing catalyst particles and subjected to steam at elevated temperatures, e.g., those present in FCC unit regenerators, are of limited effectiveness in reducing  $\text{SO}_x$  emissions. Incorporation of sufficient chromium on an alumina support to improve  $\text{SO}_x$  sorption results in undesirably increased coke and gas production. The presence of vanadium in the hydrocarbon feedstock to a catalytic cracking unit is known to have a deleterious effect on the cracking operation. For example, this vanadium, which deposits on the catalyst, tends to poison the catalyst, i.e., tends to inhibit the catalyst's ability to promote the desired cracking chemical reactions. This is one reason for the reluctance to even consider the use of vanadium in cracking operations.

U.S. Patents 4,469,589 and 4,472,267, relate to improved materials for reducing  $\text{SO}_x$  emissions comprising spinels, preferably alkaline earth metal, aluminum-containing spinels, which materials may contain one or more other metal components capable of promoting the oxidation of sulfur dioxide to sulfur trioxide at combustion conditions. Such metallic components include components of Group IB metals, Group IIB metals, Group IVB metals, Group VIA metals, Group VIB metals, Group VIIA metals, Group VIII metals, the rare earth metals, vanadium, iron, tin, antimony and mixtures thereof. In specific examples, these patents disclose that magnesium, aluminum-containing spine] is impregnated with such other metal components (e.g., cerium and platinum) using conventional techniques. In addition, these patents disclose that in situations where the spinel normally contains aluminum ions, other trivalent metal ions, such as iron, chromium, vanadium, manganese, gallium, boron, cobalt and mixtures thereof, may replace all or a part of the aluminum ions. U.S. Patents 4,471,070; 4,472,532; 4,476,245; 4,492,677; 4,492,678; 4,495,304; 4,495,305 and 4,522,937 also relate to spinel compositions useful to reduce sulfur oxide atmospheric emissions. EP-A-110 702 which corresponds to US-A-4,522,937 relates to a preparative process for alkaline earth metal, aluminum containing spinels including at least one additional metal component provided in said spinel. However, this document also suggests to add a small amount of iron for improving the effectiveness of the spinel base for pickup of  $\text{SO}_x$  and for subsequent release of sulfur. By adding of iron four metals containing spinels are achieved, whereby those spinels containing only three metals with iron as third metals best sulfate reduction values are achieved. There remains a need for still further improved spinel compositions exhibiting good  $\text{SO}_x$  removal and/or nitrogen oxide reduction properties.

In one general aspect, the present invention involves a composition, hereinafter referred to as "ROS", comprising at least one metal-containing spinel, preferably a major component of such spinel, which includes a first metal and a second metal having a valence higher than the valence of the first metal, a minor amount of at least one component of a third metal other than the first and second metals effective to promote the oxidation of sulfur dioxide to sulfur trioxide at sulfur dioxide oxidation conditions, and a minor amount of at least one component of a fourth metal other than the first, second and third metals effective to promote the reduction at first metal sulfate at first metal sulfate reduction conditions; provided that in the event the third metal is rare earth metal, the fourth metal is other than vanadium. Vanadium, rare earth metal-containing spinel compositions are disclosed and claimed in commonly assigned U.S. patent application Serial No.(Attorney Docket No. 15256). In another embodiment, the invention involves a catalyst system comprising, in intimate admixture, a major amount of solid particles capable of promoting hydrocarbon conversion at hydrocarbon conversion conditions, and a minor amount of discrete entities

having a chemical make-up which is different from the solid particles and which comprises the ROS described above. The present ROS have been found to provide for both outstanding effectiveness in removing sulfur oxides, e.g., from the catalyst regeneration zones of hydrocarbon catalytic cracking units, and improved effectiveness in releasing associated sulfur oxide, e.g., in the reaction zones of hydrocarbon catalytic cracking units. The amounts of third and fourth metals present in the ROS are preferably chosen so that the third and fourth metal components have no substantial detrimental effect on the hydrocarbon conversion, e.g., cracking process.

In a further embodiment, the invention relates to a process for reducing at least one, preferably both, of (1) the sulfur oxide content of a sulfur oxide-containing gas and (2) the nitrogen oxide content of a nitrogen oxide-containing gas which comprises contacting the gas with a material at conditions to reduce at least one of (1) the sulfur oxide content of the gas and (2) the nitrogen oxide content of the gas. The material to be used is the ROS first described above.

In yet another embodiment, the present invention relates to an improved hydrocarbon conversion, preferably cracking, process for converting a sulfur-containing hydrocarbon feedstock. The process comprises (1) contacting the feedstock with solid particles capable of promoting the conversion of the feedstock at hydrocarbon conversion conditions in at least one reaction zone to produce at least one hydrocarbon product and to cause deactivating sulfur-containing carbonaceous material to be formed on the solid particles; (2) contacting the deposit-containing particles with an oxygen-containing vaporous medium at conditions to combust at least a portion of the carbonaceous deposit material in at least one regeneration zone to thereby regenerate at least a portion of the hydrocarbon conversion catalytic activity of the solid particles and to form a regeneration zone flue gas containing sulfur oxide (e.g., sulfur trioxide) and/or nitrogen oxide; and (3) repeating steps (1) and (2) periodically. The present improvement comprises using, in intimate admixture with the solid particles, a minor amount of discrete entities having a chemical make-up which is different from the solid particles and which comprises the ROS first described above. Such discrete entities are present in an amount effective to reduce the amount of sulfur oxides and/or nitrogen oxides in the flue gas.

In one embodiment, the discrete entities also include a minor, catalytically effective amount of at least one crystalline material effective to promote hydrocarbon conversion, e.g., cracking, at hydrocarbon conversion conditions.

The preferred relative amounts of the solid particles and discrete entities are about 80 to about 99 parts and about 1 to about 20 parts by weight, respectively. This catalyst system is especially effective for the catalytic cracking of a hydrocarbon feedstock to lighter, lower boiling products. The present catalyst system also has improved carbon monoxide oxidation catalytic activity and stability.

In another embodiment, the ROS has a surface area (by the conventional B.E.T. method) in the range of 25m<sup>2</sup>/g. to 600m<sup>2</sup>/g., more preferably 40m<sup>2</sup>/g. to 400m<sup>2</sup>/g., and still more preferably 50m<sup>2</sup>/g. to 300m<sup>2</sup>/g. These relatively high surface areas have been found to provide for improved reduction in sulfur oxide and/or nitrogen oxide atmospheric emissions.

This invention can be used to advantage with the catalyst (solid particles and discrete entities) being disposed in any conventional reactor-regenerator system, in ebullating catalyst bed systems, in systems which involve continuously conveying or circulating catalyst between reaction zone and regeneration zone and the like. Circulating catalyst systems are preferred. Typical of the circulating catalyst bed systems are the conventional moving bed and fluidized bed reactor-regenerator systems. Both of these circulating bed systems are conventionally used in hydrocarbon conversion, e.g., hydrocarbon cracking, operations with the fluidized catalyst bed reactor-regenerator systems being preferred.

Although the presently useful solid particles and discrete entities may be used as a physical admixture of separate particles, in one embodiment the discrete entities are combined as part of the solid particles. That is, the discrete entities, e.g., comprising calcined microspheres of the ROS, are combined with the solid particles, e.g., during the manufacture of the solid particles, to form combined particles which function as both the presently useful solid particles and discrete entities. In this embodiment the discrete entities are preferably a separate and distinct phase in the combined particles. One preferred method for providing the combined particles is to calcine the discrete entities prior to incorporating the discrete entities into the combined particles.

The form, i.e., particle size, of the present particles, e.g., both solid particles and discrete entities as well as the combined particles, is not critical to the present invention and may vary depending, for example, on the type of reaction-regeneration system employed. Such particles may be formed into any desired shape such as pills, cakes, extrudates, powders, granules, spheres and the like, using conventional methods. Where, for example, the final particles are designed for use as a fixed bed, the particles may preferably be formed into particles having a minimum dimension of at least about 0.245 mm (0.01 inch) and

a maximum dimension of up to about 1.27 cm (one-half inch) or 2.54 cm (one inch) or more. Spherical particles having a diameter of 0.76 mm (0.03 inch) to 6.35 mm (0.25 inch), preferably 0.76 mm (0.03 inch) to 3.81 mm (0.15 inch), are often useful, especially in fixed bed or moving bed operations. With regard to fluidized systems, it is preferred that the major amount by weight of the particles have a diameter in the range of 10  $\mu\text{m}$  to 250  $\mu\text{m}$ , more preferably 20  $\mu\text{m}$  to 150  $\mu\text{m}$ .

The solid particles are capable of promoting the desired hydrocarbon conversion. By "hydrocarbon conversion" is meant a chemical reaction or conversion in which one or more of the feed materials or reactants and/or one or more of the products or conversion products is substantially hydrocarbon in nature, e.g., comprises a major amount of weight of carbon and hydrogen. The solid particles are further characterized as having a composition (i.e., chemical make-up) which is different from the discrete entities. In one preferred embodiment, the solid particles (or the solid particles portion of the combined particles described above) are substantially free of ROS.

The composition of the solid particles useful in the present invention is not critical, provided that such particles are capable of promoting the desired hydrocarbon conversion. Solid particles having widely varying compositions are conventionally used as catalyst in such hydrocarbon conversion processes, the particular composition chosen being dependent, for example, on the type of hydrocarbon chemical conversion desired. Thus, the solid particles suitable for use in the present invention include at least one of the natural or synthetic materials which are capable of promoting the desired hydrocarbon chemical conversion. For example, when the desired hydrocarbon conversion involves one or more of hydrocarbon cracking (preferably in the substantial absence of added free molecular hydrogen), disproportionation, isomerization, hydrocracking, reforming, dehydrocyclization, polymerization, alkylation and dealkylation, such suitable materials include acid-treated natural clays, such as montmorillonite, kaolin and bentonite clays; natural or synthetic amorphous materials, such as alumina, silica, silica-alumina, silica-magnesia and silica-zirconia composites; crystalline materials often referred to as zeolites or molecular sieves, such as aluminosilicates, SAPO, TAPO, MeAPO, LZ-210, LZ-10, and the like. Certain of these crystalline materials are discussed in U.S. Patents 4,310,440; 4,440,871; 4,500,651; and 4,503,023.

In certain instances, e.g., hydrocarbon cracking and disproportionation, the solid particles preferably include such crystalline materials to increase catalytic activity. Methods for preparing such solid particles and the combined solid particles-discrete entities particles are conventional and well known in the art. For example, crystalline aluminosilicate compositions can be made from alkali metal silicates and alkali metal aluminates so that they initially contain significant concentrations of alkali metals. Sodium tends to reduce the catalyst activity of the composition for hydrocarbon conversion reactions such as hydrocarbon cracking and disproportionation. Accordingly, most or all of the sodium in the crystalline aluminosilicate is removed or replaced, e.g., with other metal cations such as aluminum ions or ions of the rare earths, which are associated with the crystalline aluminosilicates. This can be accomplished by contacting the crystalline aluminosilicate with a source of hydrogen ions such as acids, or hydrogen precursors such as ammonium compounds. These procedures are thoroughly described in U.S. Patents 3,140,253 and RE. 27,639.

Compositions of the solid particles which are particularly useful in the present invention are those in which the crystalline material is incorporated in an amount effective to promote the desired hydrocarbon conversion, e.g., a catalytically effective amount, into a porous matrix which comprises, for example, amorphous material which may or may not be itself capable of promoting such hydrocarbon conversion. Included among such matrix materials are clays and amorphous compositions of alumina, silica, silica-alumina, magnesia, zirconia, mixtures of these and the like. The crystalline material is preferably incorporated into the matrix material in amounts within the range of about 1% to about 75%, more preferably about 2% to about 50%, by weight of the total solid particles. The preparation of crystalline-amorphous matrix catalytic materials is described in the above-mentioned patents. Catalytically active crystalline materials which are formed during and/or as part of the methods of manufacturing the solid particles, discrete entities and/or as part of the methods of manufacturing the solid particles, discrete entities and/or combined particles are within the scope of the present invention. The solid particles are preferably substantially free of added rare earth metal, e.g., cerium, component disposed on the amorphous matrix material of the catalyst, although such rare earth metal components may be associated with the crystalline materials of the solid particles.

The solid particles useful in the catalytic hydrocarbon cracking embodiment of the present invention may be any conventional catalyst capable of promoting hydrocarbon cracking at the conditions present in the reaction zone, i.e., hydrocarbon cracking conditions. Similarly, the catalytic activity of such solid particles is restored at the conditions present in the regeneration zone. Typical among these conventional catalysts are those which comprise amorphous silica-alumina and at least one crystalline aluminosilicate having pore diameters of 0.8 nm (8 angstroms) to 1.5 nm (15 angstroms) and mixtures thereof. When the

solid particles and/or discrete entities to be used in the hydrocarbon cracking embodiment of the present invention contain crystalline aluminosilicate, the crystalline aluminosilicate may include minor amounts of conventional metal promoters such as the rare earth metals, in particular, cerium.

As indicated above, the present ROS comprise an effective amount, preferably a major amount, of at least one spinel containing a first metal and a second metal, preferably alkaline earth metal-containing spinel, a minor amount of at least one component of a different third metal effective to promote the oxidation of sulfur dioxide to sulfur trioxide at sulfur dioxide oxidation conditions, and a minor amount of at least one component of a different fourth metal effective to promote the reduction of first metal sulfate at first metal sulfate reduction conditions. In another preferred aspect, the present ROS include amounts of third metal component and fourth metal component which are effective to promote the reduction of nitrogen oxides at nitrogen oxide reduction conditions.

The spinel structure is based on a cubic close-packed array of oxide ions. Typically, the crystallographic unit cell of the spinel structure contains 32 oxygen atoms; one-eighth of the tetrahedral holes (of which there are two per anion) are occupied by divalent metal ion, and one-half of the octahedral holes (of which there are two per anion) are occupied by trivalent metal ions.

This typical spinel structure or a modification thereof is adaptable to many other mixed metal oxides of the type  $M^{II}M_2^{III}O_4$  (e.g.,  $FeCr_2O_4$ ,  $SnAl_2O_4$  and  $Co^{II}Co_2^{III}O_4$ ), by some of the type  $M^{IV}M_2^{II}O_4$  (e.g.,  $TiSn_2O_4$ , and  $SnCo_2O_4$ ), and by some of the type  $M^{II}_2M^{VI}O_4$  (e.g.,  $Na_2MoO_4$  and  $Ag_2MoO_4$ ). This structure is often symbolized as  $X[Y_2]O_4$ , where square brackets enclose the ions in the octahedral interstices. An important variant is the inverse spinel structure,  $Y[XY]O_4$ , in which half of the Y ions are in tetrahedral interstices and the X ions are in octahedral ones along with the other half of the Y ions. The inverse spinel structure is intended to be included within the scope of the term "metal-containing spinel" as used herein. The inverse spinel structure occurs often when the X ions have a stronger preference for octahedral coordination than do the Y ions. All  $M^{IV}M_2^{II}O_4$  are inverse, e.g.,  $Sn(SnTi)O_4$ , and many of the  $M^{II}M_2^{III}O_4$  ones are also. There are also many compounds with distorted spinel structures in which only a fraction of the X ions are in tetrahedral sites. This occurs when the preference of both X and Y ions for octahedral and tetrahedral sites do not differ markedly.

Further, details on the spinel structure are described in the following references, which are hereby incorporated herein by reference: "Modern Aspects of Inorganic Chemistry" by H. I. Emeleus and A. G. Sharpe (1973), pp. 57-58 and 512-513; "Structural Inorganic Chemistry", 3rd edition, (1962) by A. F. Wells, pp. 130, 487-490, 503 and 526; and "Advanced Inorganic Chemistry", 3rd edition, by F. A. Cotton and G. Wilkinson (1972), pp. 54-55.

Metal-containing spinels include the following:  $MnAl_2O_4$ ,  $FeAl_2O_4$ ,  $CoAl_2O_4$ ,  $NiAl_2O_4$ ,  $ZnAl_2O_4$ ,  $MgTiMgO_4$ ,  $FeMgFeO_4$ ,  $FeTiFeO_4$ ,  $ZnSnZnO_4$ ,  $GaMgGaO_4$ ,  $InMgInO_4$ ,  $BeLi_2F_4$ ,  $MoLi_2O_4$ ,  $SnMg_2O_4$ ,  $MgAl_2O_4$ ,  $CuAl_2O_4$ ,  $(LiAl_5O_8)$ ,  $ZnK_2(CN)_4$ ,  $CdK_2(CN)_4$ ,  $HgK_2(CN)_4$ ,  $ZnTi_2O_4$ ,  $FeV_2O_4$ ,  $MgCr_2O_4$ ,  $MnCr_2O_4$ ,  $FeCr_2O_4$ ,  $CoCr_2O_4$ ,  $NiCr_2O_4$ ,  $ZnCr_2O_4$ ,  $CdCr_2O_4$ ,  $MnCr_2S_4$ ,  $ZnCr_2S_4$ ,  $CdCr_2S_4$ ,  $TiMn_2O_4$ ,  $MnFe_2O_4$ ,  $FeFe_2O_4$ ,  $CoFe_2O_4$ ,  $NiFe_2O_4$ ,  $CuFe_2O_4$ ,  $ZnFe_2O_4$ ,  $CdFe_2O_4$ ,  $MgCo_2O_4$ ,  $TiCo_2O_4$ ,  $CoCo_2O_4$ ,  $ZnCo_2O_4$ ,  $SnCo_2O_4$ ,  $CoCo_2S_4$ ,  $CuCo_2S_4$ ,  $GeNi_2O_4$ ,  $NiNi_2S_4$ ,  $ZnGa_2O_4$ ,  $WAg_2O_4$ , and  $ZnSn_2O_4$ .

The presently useful metal-containing spinels include a first metal and a second metal having a valence (oxidation state) higher than the valence of the first metal. The first and second metals may be the same metal or different metals. In other words, the same metal may exist in a given spinel in two or more different oxidation states. As indicated above, the atomic ratio of the first metal to the second metal in any given spinel need not be consistent with the classical stoichiometric formula for such spinel. In one embodiment, the atomic ratio of the first metal to the second metal in the metal-containing spinel useful in the present invention is at least about 0.17 and preferably at least about 0.25. If the first metal is a monovalent metal, the atomic ratio of the first metal to the second metal is preferably at least about 0.34; more preferably at least about 0.5.

The preferred metal-containing spinels for use in the present invention are alkaline earth metal spinels, in particular magnesium (first metal) and aluminum (second metal)-containing spinel. Other alkaline earth metal ions, such as calcium, strontium, barium and mixtures thereof, may replace all or a part of the magnesium ions. Similarly, other metal ions, such as iron, chromium, vanadium, manganese, gallium, boron, cobalt, Group IB metals, Group IV metals, Group VA metals, the platinum group metals, the rare earth metals, Te, Nb, Ta, Sc, Zn, Y, Mo, W, Ti, Re, U, Th and mixtures thereof, may replace all or a part of the aluminum ions, preferably only a part of the aluminum ions. When the spine] includes a divalent metal (e.g., magnesium) and a trivalent metal (e.g., aluminum), it is preferred that the atomic ratio of divalent to trivalent metals in the spine] be in the range of 0.17 to 2.5, more preferably 0.25 to 2.0, and still more preferably 0.35 to 1.5.

The metal-containing spinels useful in the present invention may be derived from conventional and well

known sources. For example, these spinels may be naturally occurring or may be synthesized using techniques well known in the art. Thus, a detailed description of such techniques is not included herein.

Substantially non-interfering proportions of other well known refractory material, e.g., inorganic oxides such as silica, zirconia, thoria and the like may be included in the present ROS. By substantially "non-interfering" is meant amounts of the material which do not have a substantial deleterious effect on the intended functionality of the present ROS, catalyst system, or hydrocarbon conversion process, as the case might be. The inclusion of materials such as silica, silica-alumina, zirconia, thoria and the like into the present ROS may act to improve one or more of the functions of these ROS. Free magnesia and/or alumina (i.e., apart from the alkaline earth metal containing spinel) also may be included in the present ROS, e.g., using conventional techniques. For example, in one embodiment the ROS preferably includes 0.1% to 30% by weight of free magnesia (calculated as MgO). Such free magnesia may act to improve the effectiveness of the ROS to reduce sulfur oxide and/or nitrogen oxide atmospheric emissions.

The third metal component and the fourth metal component may be associated with the spinel using any suitable technique or combination of techniques; for example, impregnation, coprecipitation, ion-exchange and the like, well known in the art. Thus, the third metal and fourth metal components may be an integral part of the spinel or may be in a phase separate from the spinel (e.g., deposited on the spinel) or both. These metal components may be associated with the spinel together or in any sequence or by the same or different association techniques. Cost considerations favor the preferred procedure in which the metal components are associated together with the spinel. Impregnation may be carried out by contacting the spinel with a solution, preferably an aqueous solution, of third and fourth metal salts.

The third metal component is chosen from those components effective to promote the oxidation of sulfur dioxide to sulfur trioxide at sulfur dioxide oxidation conditions. The third metal component is preferably a component of a metal selected from the group consisting of Group IB metals, Group IIB metals, Group VIA metals, the rare earth metals, the platinum group metals and mixtures thereof. More preferably, the rare earth metals, the platinum group metals and mixtures thereof. Particularly good results are achieved when the third metal is cerium and/or platinum, with cerium giving outstanding results.

The fourth metal component is chosen from those components effective to promote the reduction of first metal (e.g., magnesium) sulfate at first metal sulfate reduction conditions, such as those conditions prevailing in the typical reaction zone of a hydrocarbon fluid catalytic cracking unit. The fourth metal component is preferably a component of a metal selected from the group consisting of nickel, titanium, chromium, manganese, cobalt, germanium, tin, bismuth, molybdenum, antimony, vanadium and mixtures thereof. More preferably, the fourth metal is selected from iron, nickel, cobalt, manganese, tin, vanadium and mixtures thereof.

The specific amounts of the third and fourth metal components included in the ROS may vary widely, provided that these components are effective as described herein. Preferably, the third metal component is present in an amount between 0.001% to 20% by weight, calculated as elemental metal, of the ROS, and the fourth metal component is present in an amount between 0.001% to 10% by weight, calculated as elemental metal, of the ROS. It is preferred that excessive amounts of third and/or fourth metal components be avoided, particularly in hydrocarbon conversion applications, to reduce the risk of substantially detrimentally affecting the primary process. Preferably, the ROS include 0.1% to 20%, more preferably 0.05% to 20%, and still more preferably 2% to 15%, by weight of rare earth metal, calculated as elemental metal. Of course, if the platinum group metal is employed in the ROS, very much reduced concentrations (e.g., in the parts per million (ppm) range) are employed. If vanadium is included as the fourth metal component, it is preferably present in an amount of 0.05% to 7%, more preferably 0.1% to 5%, and still more preferably 0.2% to 2% by weight of vanadium, calculated as elemental metal.

It may not be necessary to wash the spinel after certain soluble third and fourth metal salts (such as nitrate or acetate) are added. After impregnation with the third and fourth metal salts, the spinel can be dried and calcined to decompose the salts, forming an oxide in the case of nitrate or acetate. Alternately the spinel, e.g., in the form of discrete particles, can be charged to a hydrocarbon conversion, e.g., cracking, unit with the metals in salt form. In this case, the third and fourth metal salts with thermally decomposable anions can decompose to the oxides in the unit.

The present discrete entities may further comprise a minor amount of at least one crystalline material capable of promoting the desired hydrocarbon conversion. Typical crystalline materials have been described above. Such crystalline materials may comprise 1% to 30%, for example, 1% to 10%, by weight of the discrete entities. The presence of such crystalline materials in the present discrete entities acts to increase the overall catalytic activity of the solid particles-discrete entities mixture for promoting the desired hydrocarbon conversion.

Preferably, the third and fourth metal components are substantially uniformly disposed in or on the

ROS.

Included among the rare earth metals useful in the present invention are the Lanthanum or Lanthanide Series (of the Periodic Chart of Elements) metals and mixtures thereof. The preferred rare earth metals are selected from the group consisting of cerium, praseodymium, lanthanum and mixtures thereof, with cerium being more preferred.

As noted above, the presently useful solid particles and discrete entities can be employed in a mass of combined particles which function as both the solid particles, e.g., promotes hydrocarbon conversion, and the discrete entities. Such combined particles may be produced in any suitable manner, certain of which methods are conventional and known in the art.

Although this invention is useful in many hydrocarbon conversions, the present catalyst, i.e., mixture comprising solid particles and discrete entities, and hydrocarbon conversion process find particular applicability in systems for the catalytic cracking of hydrocarbons where oxidative regeneration of catalyst is employed. Such catalytic hydrocarbon cracking often involves converting, i.e., cracking, heavier or higher boiling components, to gasoline and other lower boiling components, such as hexane, hexene, pentane, pentene, butane, butylene, propane, propylene, ethane, ethylene, methane and mixtures thereof. Often, the substantially hydrocarbon feedstock comprises a gas oil fraction, e.g., derived from petroleum, shale oil, tar sand oil, coal and the like. Such feedstock may comprise a mixture of straight run, e.g., virgin, gas oil. Such gas oil fractions often boil primarily in the range of 204°C (400 degrees F.) to 538°C (1000 degrees F.). Other substantially hydrocarbon feedstocks, e.g., naphtha, high boiling or heavy fractions of petroleum, petroleum residuum, shale oil, tar sand oil, coal and the like, may be cracked using the catalyst and method of the present invention. Such substantially hydrocarbon feedstock often contains minor amounts of other elements, e.g., sulfur, nitrogen, oxygen and the like. In one aspect, the present invention involves converting a hydrocarbon feedstock containing sulfur and/or sulfur chemically combined with the molecules of hydrocarbon feedstock. The present invention is particularly useful when the amount of sulfur in such hydrocarbon feedstock is in the range of 0.01% to 5%, preferably 0.1% to 3%, by weight of the total feedstock.

Hydrocarbon cracking conditions are well known and often include temperatures in the range of 455°C (850 degrees F.) to 593°C (1100 degrees F.), preferably 482°C (900 degrees F.) to 566°C (1050 degrees F.). Other reaction conditions usually include pressures of up to about 7.9 bar (100 psig); catalyst to oil ratios of 1 to 2 to 25 to 1, preferably 3 to 1 to 15 to 1; and weight hourly space velocities (WHSV) of 3 to 60. These hydrocarbon cracking conditions may be varied depending, for example, on the feedstock and solid particles or combined particles being used, the reactor-regenerator system, e.g., fluid or moving bed catalytic cracking system, being employed and the product or products wanted.

In addition, the catalytic hydrocarbon cracking system includes a regeneration zone for restoring the catalytic activity of the solid particles or combined particles of catalyst previously used to promote hydrocarbon cracking. Carbonaceous, in particular sulfur-containing carbonaceous, deposit-containing catalyst particles from the reaction zone are contacted with free oxygen-containing gas in the regeneration zone at conditions to restore or maintain the activity of the catalyst by removing, i.e., combusting, at least a portion of the carbonaceous material from the catalyst particles. When the carbonaceous deposit material contains sulfur, at least one sulfur-containing combustion product is produced in the regeneration zone and may leave the zone with the regenerator flue gas. The conditions at which such free oxygen-containing gas contacting takes place may vary, for example, over conventional ranges. The temperatures in the catalyst regeneration zone of a hydrocarbon cracking system are often in the range of 482°C (900 degrees F.) to 816°C (1500 degrees F.), preferably 593°C (1100 degrees F.) to 732°C (1350 degrees F.) and more preferably 593°C (1100 degrees F.) to 732°C (1300 degrees F.). Other conditions within such regeneration zone may include, for example, pressures up to about 7.9 bar (100 psig.), and average catalyst contact times within the range of 3 minutes to 75 minutes. Sufficient oxygen is preferably present in the regeneration zone to completely combust the carbon and hydrogen of the carbonaceous deposit material, for example, to carbon dioxide and water. The amount of carbonaceous material deposited on the catalyst in the reaction zone is preferably in the range of 0.005% to 15%, more preferably 0.1% to 10%, by weight of the catalyst. The amount of sulfur, if any, contained in the carbonaceous deposit material depends, for example, on the amount of sulfur in the hydrocarbon feedstock. This deposit material may contain 0.01% to 10% or more by weight of sulfur. At least a portion of the regenerated catalyst is often returned to the hydrocarbon cracking reaction zone.

One embodiment of the present invention involves contacting sulfur oxide and/or nitrogen oxide-containing gases, e.g., combustion products, with the present ROS. Reduced concentrations of sulfur oxide and/or nitrogen oxide, e.g., reduced emissions of sulfur oxide and/or nitrogen oxide from the combustion zones, are achieved as a result of this contacting.



Typical combustion zones include, for example, fluid bed coal burning steam boilers and fluid sand bed waste combustors. In the coal fired boiler application, the present ROS may be added, either separately or with the sulfur-containing coal, to the combustion zone, e.g., boiler, where combustion takes place. The present ROS then leave the combustion zone with the coal ash and can be separated from the ash, e.g., by screening, density separation, or other well known solids separation techniques. In one embodiment, the sulfur oxide-containing gases are contacted with the present ROS at conditions to reduce the sulfur oxide content of the gases in one or more zones, e.g., separate from the combustion zone. In any event, the flue gases leaving the combustion zone/contacting zone system have reduced amounts of sulfur oxide and/or nitrogen oxide, e.g., relative to processing in the absence of the present ROS. The ROS from the combustion zone or contacting zone can be subjected to a reducing environment, e.g., contacted with hydrogen, hydrocarbon and the like reducing media, at conditions such that at least a portion of the sulfur associated with the ROS is disassociated, e.g., in the form of hydrogen sulfide and is removed for further processing, e.g., sulfur recovery. The ROS, after sulfur removal may be recycled to the combustion zone or contacting zone.

Conditions within such contacting zones may be those typically used in contact zones employing conventional sulfur oxide or nitrogen oxide removal agents. The amount of the present ROS used to contact a sulfur oxide-containing and/or a nitrogen oxide containing gas is sufficient to reduce the sulfur oxide and/or nitrogen oxide content of the gas, preferably, by at least about 50% and more preferably by at least 80%. Reducing conditions are such that at least a portion, preferably at least about 50% and more preferably at least about 80% of the sulfur associated with the ROS is removed. For example, reducing conditions may include temperatures in the range of 482°C (900 degrees F.) to 982°C (1800 degrees F.); pressures in the range of 1,9 to 7,9 bar (14 to 100 psig); and reducing media, e.g., hydrogen, hydrocarbon and the like, to associated sulfur mole ratio in the range of 1 to 10.

The following examples are provided to better illustrate the invention, without limitation, by presenting several specific embodiments of the compositions processes of the invention.

#### EXAMPLES 1 TO 12

A series of magnesium, aluminum-containing spinel compositions were prepared as follows.

Magnesium, aluminum-containing spinel particles were prepared using conventional coprecipitation/calcining techniques. The resulting spinel had a surface area of more than 100m<sup>2</sup>/g. (square meters per gram); and an atomic ratio of magnesium to aluminum of 0.77. The average particle size of the spinel particles was in the range of about 65 µm.

Fourteen portions of these spinel particles were subjected to conventional impregnation/calcining techniques using aqueous solutions of various metal salts to prepare the following fourteen compositions\*:

Composition/Example	Wt. % of Metal (as Elemental Metal) Included with the Spinel Particles
Example 1	5% Cerium
Example 2	10% Cerium
Example 3	20% Cerium
Example 4	10% Praseodymium
Example 5	10% Lanthanum
Example 6	10% Iron
Example 7	10% Manganese
Example 8	10% Cobalt
Example 9	5% Vanadium
Example 10	2% Vanadium/10% Cerium
Example 11	10% Tin
Example 12	5% Tin/5% Cerium

The impregnation/calcining of the various portions of the spinel particles did not substantially change the surface area of the spinel or the size of the particles.

\* When two metals are included with the spinel particles, the spinel particles were impregnated with both metals simultaneously.

Examples 13-26

A quantity of solid particles of a commercially available, crystalline aluminosilicate hydrocarbon cracking catalyst, having the same approximate particle size distribution as the spinel-containing particles from Examples 1 to 14, was combined with each of the final products of Examples 1 to 14 so that mixtures of 1.75 parts by weight of the spinel-containing particles (discrete entities) and 98.25 parts by weight of the solid particles resulted. The catalytic activity of the solid particles was equilibrated by use (prior to combining with the discrete entities) in commercial fluid bed catalytic cracking service.

Each blend was tested to determine its ability to continue to remove sulfur oxides over a period of time. This test procedure was as follows: Step 1 involved an initial determination of the ability of the blend to remove sulfur oxides from regenerator flue gases. Step one was carried out in a fluid bed catalytic cracking pilot plant known to provide results which are correlatable to results obtained in commercial sized systems. The feedstock and conditions for step 1 were as follows:

Feedstock - mid-continent gas oil containing

about 2% by weight sulfur

Reactor temperature - 538° C (1000 degrees F.)

Regenerator temperature - 693° C (1280 degrees F.)

Stripper temperature - 499° C (930 degrees F.)

Pressure - 1,0335 bar (15 psia)

Approximate catalyst regeneration time - 30 minutes

Catalyst to oil weight ratio - 6

Weight hourly space velocity - 10

Steam as inerts in reactor, 3 mole %.

Step 2 of the test procedure involved continuous and accelerated aging in a fluidized-bed reactor to simulate the type of aging which occurs in commercial fluid-bed catalytic cracking service. The feedstock and conditions utilized in step 2 were as follows:

Feedstock - mid-continent gas oil containing

2% by weight sulfur

Reactor temperature - 566° C (1150 degrees F.)

Reactor pressure - 2,046 bar (15 psig)

Reaction catalyst/oil weight ratio - 15

Weight hourly space velocity - 0.8

Regenerator temperature - 732° C (1350 degrees F.)

Regenerator pressure - 2,046 bar (15 psig)

Catalyst regenerator residence time - 30 minutes

Regenerator combustion air flow ratio - 9.03 kg (20 lbs.) air/0.454 kg (lb.) coke

Cycles per day - 11

Step 3 of the test procedure involved periodically repeating step 1 to determine how much of the blend's activity to remove sulfur oxide had been lost during the aging of step 2.

The amount of total sulfur oxides emitted with the flue gases from the regeneration using the blend was used as the basis for determining the blend's ability (or activity) to remove such sulfur oxides.

Results of testing these blends were as follows:

	RELATIVE ACTIVITY TO REMOVE SULFUR OXIDES
Example 1 Virgin	52
Example 1 Aged 2 days	—
Example 2 Virgin	83
Example 2 Aged 2 days	32
Example 3 Virgin	83
Example 3 Aged 2 days	42
Example 4 Virgin	32
Example 4 Aged 2 days	—
Example 5 Virgin	40
Example 5 Aged 2 days	31
Example 6 Virgin	31
Example 6 Aged 2 days	—
Example 7 Virgin	36
Example 7 Aged 2 days	—
Example 8 Virgin	6
Example 8 Aged 2 days	—
Example 9 Virgin	81
Example 9 Aged 2 days	27
Example 10 Virgin	96
Example 10 Aged 2 days	78
Example 11 Virgin	less than 25
Example 11 Aged 2 days	—
Example 12 Virgin	56
Example 12 Aged 2 days	—

These data indicate clearly that compositions according to the present invention, i.e., Composition 12 have substantial initial sulfur oxide removal activity.

For example, the initial sulfur oxide removal activity of Composition 12 (5% tin/5% cerium) is increased relative to that of Composition 1 (5% cerium) or Composition 11 (10% tin). In addition, the sulfur oxide removal activity stability, i.e., the ability to maintain sulfur oxide removal activity over a period of time, of Composition 12 is increased relative to that of Composition 2.

#### Example 27

Samples of virgin and aged Composition 12 are taken from a point between the reaction zone and the regeneration zone of the above-noted catalytic cracking pilot plant and are analyzed for sulfur content. It is found that the sulfur contents of these samples are significantly lower than those of other materials, such as Compositions 1, 2 and 3. Thus, it appears that the spinel-containing discrete entities of Composition 12 have reduced sulfur contents coming out of the reaction zone. This, in turn, provides each of the Composition 12 with an increased kinetic driving force for sulfur oxide removal in the regeneration zone.

#### Example 28

Composition 12 is tested to determine its ability to reduce the nitrogen oxide (NO<sub>x</sub>) content of the flue gases from a cracking catalyst regeneration zone. Thus, a sample of each of these blends is subjected to twenty two reaction/regeneration cycles using step (2) of the test procedure set forth above in Examples 13 to 26. After this aging, the blend is tested in accordance with step (1) of the above-noted test procedure and the nitrogen oxide content of the regeneration zone flue gases is measured. Results of these tests indicate that Composition 12 according to the present invention do provide for reduction in nitrogen oxide emissions from combustion zone flue gases.

#### Claims

1. A composition of matter comprising
  - a) at least one metal-containing spinel which includes a first metal and a second metal having a valence higher than the valence of said first metal,

- b) a minor amount of at least one component of a third metal other than said first and second metal effective to promote the oxidation of sulfur dioxide to sulfur trioxide at sulfur dioxide oxidation conditions selected from the group consisting of Group IB metals, Group IIB metals, Group VIA metals, the rare earth metals, the Platinum Group metals and mixtures thereof, and
- 5 c) a minor amount of at least one component of a fourth metal other than said first, second and third metals effective to promote the reduction of first metal sulfate at first metal sulfate reduction conditions selected from the group consisting of nickel, titanium, chromium, manganese, cobalt, germanium, tin, bismuth, molybdenum, antimony, vanadium and mixtures thereof, provided that in the event said third metal is rare earth metal, said fourth metal is other than vanadium, and wherein
- 10 said third metal component and said fourth metal component are present in amounts effective to promote the reduction of nitrogen oxides at nitrogen oxide reduction conditions.
2. The composition of claim 1 wherein said spinel has a surface area in the range of 25m<sup>2</sup>/g to 600m<sup>2</sup>/g
- 15 3. The composition of claim 2 wherein said composition comprises a major amount by weight of said spinel.
4. The composition of one of claims 1 to 3 wherein at least one of said third metal component and said fourth metal component is incorporated in said composition by impregnation.
- 20 5. The composition of one of claims 1 to 4 wherein said spinel comprises alkaline earth metal-containing spinel and the atomic ratio of said first metal to said second metal is at least 0.17.
6. The composition of claim 1 wherein said third metal is selected from the group consisting of the rare earth metals, the platinum group metals and mixtures thereof.
- 25 7. The composition of claim 1 wherein said fourth metal is selected from the group consisting of nickel, cobalt, manganese, tin, vanadium and mixtures thereof.
- 30 8. The composition of one of the foregoing claims wherein said third metal component is present in an amount in the range of 0.001% to 20% by weight, calculated as elemental third metal, and said fourth metal component is present in an amount in the range of 0.001% to 10% by weight, calculated as elemental fourth metal.
- 35 9. The composition of one of the foregoing claims wherein said spinel includes magnesium as said first metal and aluminum as said second metal, and the atomic ratio of magnesium to aluminum in said spinel is at least 0.25.
- 40 10. The composition of one of the foregoing claims further comprising 0.1% to 30% by weight of free magnesia, calculated as MgO.
11. The composition of one of the foregoing claims wherein said third metal is selected from the group consisting of cerium, platinum and mixtures thereof, and said fourth metal is selected from the group consisting of nickel, vanadium and mixtures thereof.
- 45 12. A process for reducing at least one of (1) the sulfur oxide content of a sulfur oxide-containing gas and (2) the nitrogen oxide content of a nitrogen oxide-containing gas which comprises contacting said gas with a material comprising at least one metal-containing spinel composition according to one of claims 1 to 11.
- 50 13. A composition of matter comprising, in intimate admixture, a major amount of solid particles capable of promoting hydrocarbon conversion at hydrocarbon conversion conditions, and a minor amount of discrete entities having a chemical make-up different from said solid particles and comprising at least one metal-containing spinel composition according to one of claims 1 to 11.
- 55 14. The composition of claim 13 wherein said hydrocarbon conversion comprises hydrocarbon cracking in the substantial absence of added molecular hydrogen, at least one of said solid particles and discrete entities includes crystalline aluminosilicate effective to promote said hydrocarbon cracking and a major

amount by weight of said solid particles have diameters in the range of 10  $\mu\text{m}$  to 250  $\mu\text{m}$ .

15. A hydrocarbon conversion process for converting a sulfur-containing hydrocarbon feedstock which comprises (1) contacting said feedstock with solid particles capable of promoting the conversion of said feedstock at hydrocarbon conversion conditions in at least one reaction zone to produce at least one hydrocarbon product and to cause deactivating sulfur-containing carbonaceous material to be formed on said solid particles thereby forming deposit-containing particles; (2) contacting said deposit-containing particles with an oxygen-containing vaporous medium at conditions to combust at least a portion of said carbonaceous deposit material in at least one regeneration zone to thereby regenerate at least a portion of the hydrocarbon conversion catalytic activity of said solid particles and to form a regeneration zone flue gas containing sulfur oxide and/or nitrogen oxide; and (3) repeating steps (1) and (2) periodically, characterized in that, in intimate admixture with said solid particles, a minor amount of discrete entities is used, comprising at least one metal-containing spinel composition according to one of claims 1 to 11.
16. The process of claim 15 wherein said hydrocarbon conversion comprises hydrocarbon cracking in the substantial absence of added molecular hydrogen, at least one of said solid particles and discrete entities include a crystalline aluminosilicate effective to promote said hydrocarbon cracking, a major amount, by weight of said solid particles have diameters in the range of 10  $\mu\text{m}$  to 250  $\mu\text{m}$  and said third and fourth metal components have no substantial detrimental effect on said hydrocarbon cracking.

#### Patentansprüche

1. Eine Stoffzusammensetzung enthält
  - a) mindestens ein metallhaltiges Spinell, welches ein erstes Metall beinhaltet und ein zweites Metall, das eine höhere Valenz aufweist als das erstgenannte Metall,
  - b) einen geringen Anteil an mindestens einer Komponente eines dritten Metalls, das gegenüber dem ersten und zweiten Metall wirksam die Oxidation von Schwefeldioxid zu Schwefeltrioxid unter Schwefeldioxidoxidiationsbedingungen fördert, welches aus der den Metallen der Gruppe IB, den Metallen der Gruppe IIB, den Metallen der Gruppe IVA, den Seltenerdmetallen, den Metallen der Platingruppe und Mischungen dieser Metalle bestehenden Gruppe ausgewählt ist und
  - c) einen geringen Anteil an mindestens einer Komponente eines vierten Metalls, anders als das erste, zweite und dritte Metall, das wirkungsvoll die Reduktion des ersten Metallsulfats unter Reduktionsbedingungen dieses Erstmetallsulfats ermöglicht, wobei es aus der aus Nickel, Titan, Chrom, Mangan, Cobalt, Germanium, Zinn, Wismuth, Molybdän, Antimon, Vanadium und Mischungen dieser Metalle bestehenden Gruppe ausgewählt ist. Vorausgesetzt daß in der Folge das besagte dritte Metall ein Seltenerdmetall ist und besagtes viertes Metall ein anderes als Vanadium ist und worin besagte dritte und vierte Metallkomponente in Anteilen vorhanden sind, um wirksam die Reduktionen von Stickstoffoxiden unter Stickstoffoxidreduktionsbedingungen zu fördern.
2. Die Zusammensetzung nach Anspruch 1, worin besagtes Spinell eine Oberfläche im Bereich von 25  $\text{m}^2/\text{g}$  bis 600  $\text{m}^2/\text{g}$  aufweist.
3. Die Zusammensetzung nach Anspruch 2, worin die erwähnte Stoffzusammensetzung zu einem Gewichtshauptanteil aus erwähntem Spinell besteht.
4. Die Zusammensetzung nach einem der Ansprüche 1 bis 3, worin mindestens eine der erwähnten dritten Metallkomponente und vierten Metallkomponente in die Zusammensetzung durch Imprägnierung eingelagert ist.
5. Die Zusammensetzung nach einem der Ansprüche 1 bis 4, worin das erwähnte Spinell aus einem Erdalkalimetall enthaltenden Spinell besteht und ein Atomverhältnis von besagtem ersten Metall zum zweiten Metall von mindestens 0,17 aufweist.
6. Die Zusammensetzung nach Anspruch 1, worin das erwähnte dritte Metall aus der aus Seltenerdmetallen und Metallen der Platingruppe und Mischungen dieser Metalle bestehenden Gruppe ausgewählt wird.

7. Die Zusammensetzung nach Anspruch 1, worin das vierte Metall aus der aus Nickel, Cobalt, Mangan, Zinn, Vanadium und Mischungen dieser Metalle bestehenden Gruppe ausgewählt wird.
8. Die Zusammensetzung nach einem der vorhergehenden Ansprüche, worin die erwähnte dritte Metallkomponente in einem Anteil vorhanden ist, der im Bereich von 0,001 Gew.% bis 20 Gew.%, berechnet auf das elementare dritte Metall, vorhanden ist und besagte vierte Metallkomponente in einem Bereich von 0,001 Gew.% bis 10 Gew.% vorhanden ist, berechnet auf das elementare vierte Metall.
9. Die Zusammensetzung nach einem der vorhergehenden Ansprüche, worin das Spinell Magnesium als erstes Metall und Aluminium als zweites Metall beinhaltet und das Atomverhältnis von Magnesium zu Aluminium im erwähnten Spinell mindestens 0,25 beträgt.
10. Die Zusammensetzung nach einer der vorhergehenden Ansprüche, worin ferner freies Magnesia mit 0,1 Gew.% bis 30 Gew.%, berechnet als MgO, enthalten ist.
11. Die Zusammensetzung nach einem der vorhergehenden Ansprüche, worin das dritte Metall aus der aus Cer, Platin und Mischungen dieser Metalle bestehenden Gruppe ausgewählt wird und besagtes viertes Metall aus der aus Nickel, Vanadium und Mischungen dieser Metalle bestehenden Gruppe ausgewählt wird.
12. Ein Prozess zur Reduktion von mindestens (1) dem Schwefeloxidanteil eines Schwefeloxid enthaltenden Gases und (2) den Stickstoffoxidanteil eines Stickstoffoxid enthaltenden Gases, daß das Kontaktieren des Gases mit einem Material enthält, das mindestens eine metallhaltige Spinellzusammensetzung gemäß den Ansprüchen 1 bis 10 enthält.
13. Eine Stoffzusammensetzung derart, daß in wesentlicher Beimischung ein Hauptanteil an festen Partikeln, der fähig ist Kohlenwasserstoffumsetzung unter Kohlenwasserstoffumsetzungsbedingungen durchzuführen und ein geringer Anteil von diskreten Mengen, die eine chemische Aufmachung haben, so daß sie sich von den genannten festen Partikeln unterscheiden und die mindestens eine metallhaltige Spinellzusammensetzung gemäß den Ansprüchen 1 bis 11 enthält.
14. Die Zusammensetzung nach Anspruch 13, worin die erwähnte Kohlenwasserstoffumsetzung, die Kohlenwasserstoffcracken im wesentlichen in der Abwesenheit von zugeführtem Wasserstoff versteht, mindestens erwähnte feste Partikel und diskrete Mengen, die kristallines Aluminiumsilikat enthalten, die die besagte Kohlenwasserstoffspaltung effektiv fördern und ein Hauptgewichtsanteil an besagten festen Partikeln, die einen Durchmesser in einem Bereich von 10 µm bis 250 µm aufweisen.
15. Ein Kohlenwasserstoffumwandlungsprozeß zur Umwandlung von schwefelhaltigem Kohlenwasserstoffausgangsmaterial, welches (1) Kontaktieren des besagten Ausgangsmaterials mit festen Partikeln umfasst, die fähig sind die Umsetzung des besagten Ausgangsmaterials unter Kohlenwasserstoffumsetzungsbedingungen durchzuführen, in mindestens einer einer Reaktionszone, um mindestens ein Kohlenwasserstoffprodukt herzustellen, und die Desaktivierung von schwefelhaltigem, kohlenstoffhaltigem Material einzuleiten, das sich an den festen Partikeln bildet und dadurch zur Ausbildung von ablagerungsenthaltenden Partikeln führt; (2) kontaktieren besagter ablagerungsenthaltender Partikel mit einem sauerstoffhaltigen gasförmigen Medium unter Bedingungen, um das Verbrennen von mindestens einem Teil von besagtem kohlenstoffhaltigem Ablagerungsmaterial in mindestens einer Regenerationszone durchzuführen, um dadurch mindestens einen Teil der katalytischen Kohlenwasserstoffumsetzungsaktivität von den besagten festen Partikeln zu regenerieren und eine Regenerationszone mit Rauchgas zu bilden, die Schwefeloxide und/oder Stickoxide enthalten und (3) wiederholende Schritte (1) und (2) die periodisch, charakterisiert in der Weise, unter wesentlicher Beimischung von besagten festen Partikeln, benötigt wird ein kleiner Anteil von diskreten Mengen, die mindestens eine metallhaltige Spinell-Zusammensetzung enthalten gemäß einem der Ansprüche 1 bis 11 enthält.
16. Der Prozeß nach Anspruch 15, worin die besagte Kohlenwasserstoffumwandlung eine Kohlenwasserstoffspaltung, im wesentlichen unter Abwesenheit von zugeführtem Wasserstoff enthält, aber mindestens besagte feste Partikel und eine diskrete Menge enthält, die kristallinem Aluminiumsilikat enthält, das effektiv die Kohlenwasserstoffspaltung fördern kann, ein Hauptgewichtsanteil an erwähnten festen Partikeln mit einem Durchmesser im Bereich von 10 µm bis 250 µm und das besagte dritte und vierte

Metall-Komponenten keinen wesentlichen schädlichen Effekt auf besagte Kohlenwasserstoffspaltung haben.

# Revendications

5

## 1. Composition de matière, comprenant :

- (a) au moins un spinelle contenant des métaux contenant un premier métal et un deuxième métal ayant une valence supérieure à la valence du premier métal,
- 10 (b) une quantité mineure d'au moins un composant dérivé d'un troisième métal autre que les premier et deuxième métaux, efficace pour favoriser l'oxydation du bioxyde de soufre en trioxyde de soufre dans des conditions d'oxydation du bioxyde de soufre, choisi parmi les métaux du groupe IB, les métaux du groupe IIB, les métaux du groupe VIA, les métaux de terre rare, les métaux du groupe de platine et les mélanges de ceux-ci, et
- 15 (c) une quantité mineure d'au moins un composant dérivé d'un quatrième métal autre que les premier, deuxième et troisième métaux, efficace pour favoriser la réduction du sulfate de premier métal dans des conditions de réduction du sulfate de premier métal, choisi parmi le nickel, le titane, le chrome, le manganèse, le cobalt, le germanium, l'étain, le bismuth, le molybdène, l'antimoine, le vanadium et les mélanges de ceux-ci, à condition que dans le cas où le troisième métal est un métal de terre rare, ce quatrième métal soit autre que le vanadium, et le composant dérivé du
- 20 troisième métal ainsi que le composant dérivé du quatrième métal étant présents selon des quantités efficaces pour favoriser la réduction des oxydes d'azote dans des conditions de réduction des oxydes d'azote.

25 2. Composition selon la revendication 1 dans laquelle ledit spinelle a une surface spécifique de 25 à 600 m<sup>2</sup>/g.

3. Composition selon la revendication 1, comprenant une majeure proportion en poids dudit spinelle.

30 4. Composition selon l'une des revendications 1 à 3, dans laquelle au moins l'un des composants dérivés des troisième et quatrième métaux, est incorporé dans la composition par imprégnation.

5. Composition selon l'une des revendications 1 à 4, dans laquelle le spinelle comprend un spinelle contenant un métal alcalino-terreux, le rapport atomique du premier métal au deuxième métal, étant d'au moins 0,17.

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6. Composition selon la revendication 1, dans laquelle le troisième métal est choisi parmi les métaux de terre rare, les métaux du groupe du platine et les mélanges de ceux-ci.

40 7. Composition selon la revendication 1, dans laquelle le quatrième métal est choisi parmi le nickel, le cobalt, le manganèse, l'étain, le vanadium et les mélanges de ceux-ci.

8. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composant dérivé du troisième métal est présent selon une quantité de 0,001 % à 20 % en poids d'après calcul par rapport au troisième métal sous la forme d'élément, et dans laquelle le composant dérivé du

45 quatrième métal est présent selon une quantité de 0,001 % à 10 %, d'après calcul par rapport au quatrième métal sous la forme d'élément.

9. Composition selon l'une quelconque des revendications précédentes, dans laquelle le spinelle comprend du magnésium en tant que le premier métal et de l'aluminium en tant que le deuxième métal, le rapport atomique du magnésium à l'aluminium dans ce spinelle étant d'au moins 0,25.

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10. Composition selon l'une quelconque des revendications précédentes, comprenant en outre de 0,1 % à 30 % en poids d'oxyde de magnésium libre d'après calcul sous la forme de MgO.

55 11. Composition selon l'une quelconque des revendications précédentes, dans laquelle le troisième métal est choisi parmi le cérium, le platine et les mélanges de ceux-ci, et dans laquelle le quatrième métal est choisi parmi le nickel, le vanadium et les mélanges de ceux-ci.

12. Procédé de réduction d'au moins une teneur choisie parmi (1) celle en oxyde de soufre dans un gaz contenant des oxydes de soufre et (2) celle en oxyde d'azote dans un gaz contenant des oxydes d'azote, selon lequel on met en contact ce gaz avec une matière comprenant au moins une composition à base de spinelle contenant des métaux selon l'une des quelconques des revendications 1 à 11.
13. Composition de matière comprenant, en mélange intime, une majeure proportion de particules solides capables de favoriser la conversion d'hydrocarbure dans des conditions de conversion d'hydrocarbure, et une quantité mineure d'entités discrètes ayant une composition chimique différente de celle des particules solides et comprenant au moins une composition à base de spinelle contenant des métaux selon l'une quelconque des revendications 1 à 11.
14. Composition selon la revendication 13, dans laquelle la conversion d'hydrocarbure comprend le craquage hydrocarbure pratiquement en l'absence d'hydrogène moléculaire ajouté, au moins l'un des composants choisis parmi les particules solides et les entités discrètes comprenant un aluminosilicate cristallin efficace pour favoriser ce craquage hydrocarbure, et une majeure proportion en poids de ces particules solides ayant un diamètre de 10  $\mu\text{m}$  à 250  $\mu\text{m}$ .
15. Procédé de conversion d'hydrocarbure, pour convertir une charge de départ hydrocarbonée contenant du soufre, selon lequel (1) on met en contact cette charge de départ avec des particules solides capables de favoriser la conversion de la charge de départ, dans des conditions de conversion d'hydrocarbure, dans au moins une zone réactionnelle, en formant au moins un produit hydrocarboné et en désactivant la matière carbonée sulfurée formée sur les particules solides pour constituer ainsi les particules contenant un dépôt ; (2) on met en contact ces particules contenant un dépôt avec un agent en phase vapeur contenant de l'oxygène, dans des conditions appropriées pour brûler au moins une partie du dépôt carboné, dans au moins une zone de régénération, de façon à régénérer ainsi au moins une partie de l'activité du catalyseur de conversion d'hydrocarbure de ces particules solides, et pour former un gaz de combustion issu de la zone de régénération, contenant des oxydes de soufre et/ou des oxydes d'azote ; et (3) on répète périodiquement les étapes (1) et (2) ; caractérisé en ce qu'on emploie, en mélange intime avec ces particules solides, une proportion mineure d'entités discrètes, comprenant au moins une composition à base de spinelle contenant des métaux, selon l'une quelconque des revendications 1 à 11.
16. Procédé selon la revendication 14, dans lequel la conversion d'hydrocarbure comprend le craquage d'un hydrocarbure pratiquement en l'absence d'hydrogène moléculaire ajouté, au moins un composant choisi parmi les particules solides et les entités discrètes comprenant un aluminosilicate cristallin efficace pour favoriser ce craquage d'hydrocarbure, une proportion majeure en poids de ces particules solides ayant un diamètre de 10  $\mu\text{m}$  à 250  $\mu\text{m}$ , et les composants dérivés des troisième et quatrième métaux n'ayant pratiquement pas d'effet nuisible sur ce craquage d'hydrocarbure.